Fate, accumulation and impact of metallic nanomaterials in the terrestrial environment

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Jokulsarlon, Iceland, 2018

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Chapter 6

General Discussion

The rapid increase in the manufacturing and application of engineered nanoparticles (NPs) is raising concerns on their release into the environment. A large part of the released NPs is expected to accumulate in soil, which results in an increasing concern about their negative impacts in soil ecosystems, especially in the soil-plant system[315,30,34]. Understanding the impacts of NPs on plants is of utmost importance for the ecotoxicity assessment of NPs, since plants can serve as a bridge to connect the underground components (e.g. soil bacteria) and higher-level consumers. Within this PhD I aimed to investigate the uptake, translocation and impacts of metallic NPs in plants and potentially in terrestrial food chains under different exposure scenarios. Within these studies there was a specific focus on distinguishing the relative contribution of the nanoparticulate versus the released ionic form from metallic NPs to the overall toxicity in plants. Importantly, the majority of studies on the NPs and plants are short term experiments. We conducted long(er) term exposures in order to partially fill up the associated knowledge gap on adverse effects after longer term exposure. Within these experiments we incorporated the exposure routes, exposure dynamics and physicochemical properties of NPs to study their fate, accumulation and phytotoxicity in plants. Finally, we investigated the long-term impacts of NPs on the rhizosphere soil bacterial community and their potential transfer and biomagnification into a terrestrial food chain.

In this final chapter I will first answer the research questions formulated in chapter 1, which have been addressed in Chapters 2-5:

1. How does the exposure pathway affect the uptake, translocation, and phytotoxicity of AgNPs in plants? (Chapter 2 and 4)

2. How do the shape, size and coating of NPs affect the fate, accumulation and phytotoxicity of AgNPs? (Chapter 2 and 3)

3. What is the relative contribution of the nanoparticulate and the released ionic form to the overall toxicity of suspensions of NPs and on metal accumulation in plants? (Chapter 2 and 3)

4. How and to what magnitude does the dynamic dissolution of AgNPs in soil affect their bioavailability to plants? (Chapter 4)

5. How does the soil rhizosphere bacterial community respond to exposure to AgNPs, and does this response change over time? (Chapter 4)

6. How does a mixture of AgNPs and TiO_2NPs affect the transfer of the individual NPs along a terrestrial food chain of lettuce-snails and the associated impacts on the consumer? (Chapter 5)

I will first briefly highlight the main findings of my thesis, and subsequently provide implications for environmental risk assessment and the agricultural application of NPs. I will also give an outlook and recommendations for future research here.

6.1 Answers to the research questions

6.1.1 How does the exposure pathway affect the uptake, translocation, and phytotoxicity of AgNPs in plants? (Chapter 2 and 4)

A higher reduction of the biomass of plants and stronger oxidative stress and alterations of the activities of enzymatic antioxidants in lettuce were observed following root exposure as compared to foliar exposure. This indicates that root exposure induced more phytotoxicity than foliar exposure at equal exposure concentrations. Additionally, exposure pathway-specific uptake and translocation of AgNPs was observed as well. The Ag uptake in the exposed tissue of plants for root exposure to AgNPs is higher than in the case of foliar exposure to AgNPs, whereas the translocation of Ag inside the plants from the exposed part to the unexposed part is more efficient following foliar exposure rather than following root exposure. Furthermore, soil exposure of AgNPs to plants was much less toxic compared to hydroponic exposure due to the lower bioavailability of AgNPs in soil.

6.1.2 How do the shape, size and coating of NPs affect the fate, accumulation and phytotoxicity of AgNPs? (Chapter 2 and 3)

The dissolution of AgNPs in Hoagland solution was found to be shape and coating–dependent but size-independent. The dissolution extent of silver nanospheres was higher than for the silver nanowires, and dissolution rates of uncoated silver nanowires were higher than dissolution rates of coated Ag nanowires. Additionally, the phytotoxicity and accumulation of AgNPs in plants were also shape-dependent.

Specifically, exposure to Ag nanospheres resulted in higher phytotoxicity in plants as compared to exposure to Ag nanowires. Further, the phytotoxicity and Ag accumulation in plants of the tested Ag nanowires was diameter (size) dependent, but coating independent. Exposure to the smaller sized silver nanowires induced more phytotoxicity and higher Ag accumulation in plants. This could be caused by the fact that AgNPs with smaller diameters might easier pass through the pores in/between cell walls due to the size exclusion limit of cell walls and/or apoplast, and hence induce higher toxicity[68].

6.1.3 What is the relative contribution of the nanoparticulate and the released ionic form to the overall toxicity of suspensions of NPs and on metal accumulation in plants? (Chapter 2 and 3)

According to the response addition model, we observed that nanoparticulate Ag ($NPs_{(particle)}$) was the predominant driver/descriptor of the overall toxicity and Ag accumulation in the plants rather than the released ionic Ag ($NPs_{(ion)}$) forms, as $NPs_{(particle)}$ accounted for more than 65% of the overall toxicity in all exposure scenarios. However, the relative contribution of $NPs_{(particle)}$ versus $NPs_{(ion)}$ to the overall effects was influenced by the exposure concentration and the extent of dissolution of the Ag nanowires. The contributions of dissolved ions to the overall toxicity of AgNPs suspensions showed an increasing tendency upon increasing exposure concentration. In addition, the contribution of $NPs_{(ion)}$ to the overall effects in AgNPs with a high dissolution ability was higher than in the cases of AgNWs with a low dissolution ability.

6.1.4 How and to what magnitude does the dynamic dissolution of metallic NPs in soil affect their bioavailability to plants? (Chapter 4)

Our results revealed that the extractable Ag from AgNPs amended soil increased with the increasing exposure concentration and changed over time as a result of the continuous dissolution and uptake of AgNPs by the plants. The pattern of Ag concentration in plant roots changing over time was similar to the change of the extractable Ag in the rhizosphere soil over time. Furthermore, the Spearman correlation demonstrated that the amount of Ag accumulated in the plant root and the shoots were correlated positively with DTPA-extracted Ag in the soil. These results show the important role of the dissolution of AgNPs in soil in influencing their bioavailability.

6.1.5 How does the soil rhizosphere bacterial community respond to exposure to AgNPs, and does this response change over time? (Chapter 4)

We found that the alterations in the structure and composition of the rhizosphere soil bacterial community varied over time. For the short-term exposure (7d), we did not observe any significant impact of AgNPs on the rhizosphere bacterial community regardless of exposure concentration. However, after long-term exposure (63d) to 50 mg/kg AgNPs, the decrease of the Shannon index, the separation of the bacterial community from the control and a total of 16 significantly changed featured taxa were observed. The alterations in the rhizosphere soil bacterial community were potentially associated with the abundance changes in the bacterial groups related to element (e.g., N and S) cycling and stress tolerance.

6.1.6 How does a mixture of AgNPs and TiO_2NPs affect the NPs transfer of the individual NPs along a terrestrial food chain of lettuce-snails and the associated impacts on the consumer? (Chapter 5)

We found that both Ag and Ti could be transferred from lettuce leaves to snails with trophic transfer factors (TTFs) of 0.2 to 1.1 for Ag and 4.7 to 49 for Ti when lettuce was exposed to either AgNPs or TiO_2NPs via the root. Moreover, the majority of Ag captured by snails in the AgNPs-containing treatments was excreted via the feces, whereas more than 70 % of Ti was distributed in the digestive gland of snails in the TiO_2NPs-containing treatments. In addition, treatment of snails with TiO_2NPs contaminated leaves strongly affected their feces excretion whereas AgNPs strongly affected their activity (expressed as the average BSS). Furthermore, the concurrent application of AgNPs and TiO_2NPs induced more severe inhibition of the growth and activity of snails but did not affect the biomagnification and distribution patterns of Ag and Ti in snails as compared to the application of AgNPs or TiO_2NPs alone.

6.2 Implications for risk assessment

6.2.1 Implications for environmental risk assessment

In the public consultation "Towards a Strategic Nanotechnology Action Plan (SNAP) 2010-2015", the European Commission highlighted four priority thematic areas of nanosafety research in the near future: 1) material identification and classification; 2) exposure and transformation; 3) hazard mechanisms including both human toxicology and ecotoxicology; and 4) risk prediction tools including databases and ontologies[316]. The observations in this thesis improve the understanding of the second and third issues described above by 1) investigating the fate, accumulation and impacts of metallic NPs in soil-plant systems and food chain, and 2) differentiating the main driver of toxicity of the particulate and the dissolved ionic forms. Also, our results can partly contribute to set up the ecotoxicological database of NPs, which is associated with the fourth issue of risk prediction tools including databases and ontologies as proposed by SNAP.

Our findings advance the understanding of exposure and transformation of NPs by providing novel data on the interactions between metallic NPs and terrestrial biota. **First**, we found that root exposure of AgNPs induced higher toxicity and different biodistribution patterns of Ag in plants compared to foliar exposure. The results regarding the effects of exposure pathway on plants improve the risk evaluation of metallic NPs exposure related to intentionally added applications in agriculture as well as unintentionally exposures from air-born emissions and soil emissions.

Secondly, we incorporated the dynamic exposure processes including the time-dependent dissolution and sedimentation profiles of NPs in the exposure medium into the risk assessment of metallic NPs. The dissolution and sedimentation of NPs were found to largely and dynamically affect their effective exposure concentrations and hence affect their biological impacts. As a result we showed that the EC_{25} and EC_{50} values of AgNPs to lettuce based on the time-weighted exposure concentration (incorporating the dynamic exposure conditions) were lower than the EC_{25} and EC_{50} values based on the initial exposure concentration (considering exposure as being static and hence ignoring dissolution and sedimentation). Therefore, this highlights

6

the importance of incorporating dynamic processes when evaluating the impacts of NPs on organisms to gain a more accurate and realistic assessment of NPs toxicity.

Thirdly, we distinguished the main driver for the impacts of NPs and the mode of actions of the nanoparticulate form and the released ionic form. The results demonstrate that the toxic effects of AgNPs are dramatically underestimated if there is only a focus on the impacts of dissolved ionic forms from metallic NPs alone. Also, the findings facilitate the mechanistic understanding of interactions between NPs and biological systems.

Fourthly, we quantified the toxicokinetic parameters of dissolved versus particulate forms of Ag nanowires associated with different physicochemical properties. This information is valuable for facilitating the establishment of toxicokinetic models to predict the accumulation and toxicity of NPs in higher plants. Moreover, we demonstrated that it is key to assess the actual time-related process of particles and ions in their uptake and toxicity to organisms.

Finally, we carried out the chronic exposure of NPs under more realistic exposure scenarios, such as assessing the transfer and toxicity of NPs in a microcosm consisting of the soil-lettuce-rhizosphere bacterial community as well as in a simulated terrestrial food chain of lettuce to snails. Our results clearly showed an upwards transfer of NPs in the terrestrial ecosystem from soil to plants and to snails, and a downward impact on the soil rhizosphere bacterial community. This highlights the potential risks of NPs in the terrestrial ecosystem. Importantly, we did not observe any significant impact of AgNPs on the rhizosphere bacterial community in short-term exposure, but long-term exposure to a high concentration of AgNPs indeed altered the structure and composition of the rhizosphere bacterial community. This indicates the importance of taking the long-term application of nanoparticles into account to better understand the ecological risks of nanoparticles in terrestrial ecosystems. The confirmed trophic transfer of NPs along the food chain emphasizes the importance of considering trophic transfer as a potential pathway for exposure of terrestrial herbivores to nanoparticles, especially given the increasing likelihood of application of nanoparticles in agriculture and soil remediation.

Overall, the findings of this thesis highlight the importance of 1) taking the intrinsic *properties and exposure modes of the NPs into consideration for accurate assessment of their ecotoxicological impacts, 2) considering the long term time-resolved dynamics of organisms in response to nanoparticle exposure, and 3) investigating the accumulation and translocation of NPs in organisms for environmental risk assessment of NPs.*

6.2.2 Implications for agriculture

The loss of global crop production induced by pests and diseases and the growing food requirements as a result of the burgeoning global population are the major challenges faced by the agricultural sector, especially in developing countries[2,15]. This encourages the application of nanotechnology in agriculture to increase crop production and prevent the loss of global crop production induced by pest and diseases. To date, several metallic NPs have been applied in agriculture as nano-fertilizer (e.g Cu-based nano-agrochemicals), nano-pesticide (e.g AgNPs) or nano-carrier for delivery of agrochemicals to improve the use efficiency and to enhance crop productivity[15,317]. However, the application of NPs in agriculture not only brings benefits (including increased crop production and decreased application dose of pesticides), but potentially also presents adverse effects on the function and stability of the terrestrial ecosystem. As revealed by our findings, the impacts of NPs on plants depend on the application conditions such as the application dose, exposure duration and application method, as well as on the physicochemical properties of NPs. For example, we have shown that nanowires and larger sized AgNPs are less toxic compared to nanospheres and smaller sized AgNPs. These findings exemplify the potential of enabling the industry to optimize the desired properties of AgNPs with the aim of reducing unwanted side effects within the environment whilst preserving their basic functionalities. This is an important step to achieve "green and clean" claims that are a common requirement for novel materials nowadays. In addition, the exposure pathway determines how and to what extent the NPs can enter and translocate inside plants due to the size limitations of the xylem and the phloem. Future design of environmentally friendly nano-agrochemicals should also include this information. Moreover, we observed the slow but continuing dissolution of AgNPs in soil over a period of 63 days. This information can provide sustained antimicrobial effects against plant pathogens. This implies that repeated applications of AgNP are not needed, which likely diminishes the total Ag load applied. However, we observed a relatively high amount of Ag in plant roots and the long-term disruptions of the composition of the rhizosphere bacterial community by Ag. Further, we confirmed the trophic transfer of NPs from lettuce to snails and associated negative impacts on snails. The findings highlights the potential risk of NPs being transferred to humans through the supply of crops treated with nano-agrochemicals. All these negative findings call for more attention that should be paid to balance between the potential negative effects of nano-agrochemicals and their implications in agriculture before their field application. Collaborative research among ecotoxicologists, agriculturists, physicists, chemists, material scientists and biologists is needed, as well as between the scientific community and industry to develop environmentally-friendly, efficient, mass-produced and cost-effective nano-agrochemicals that can actually get the label "green and clean".

6.3 Future research in nanoecotoxicology

Based on my research I want to provide advice on key research areas which need to be addressed in future studies to move this research field forward. Three of these area relate to the development of better analytical techniques, and another three focus on improved and more realistic toxicity testing.

6.3.1 Development in analytical techniques

The adequate detection and characterization of NPs in environment and biota are important for the accurate and comprehensive risk assessment of NPs, this section therefore addresses current challenges in the analytical techniques of NPs and the necessity of developing advanced analytical techniques.

1) Knowing the actual NPs concentrations in environmental compartments is a key prerequisite for the effective environmental risk assessment of NPs. Unfortunately, the current methods for the accurate detection, identification and quantification of NPs in environmental samples are still not optimal. ICP-MS based techniques, such as single-particle ICP-MS are being developed for quantifying the concentration of non-soluble metal-based nanospheres (e.g., AuNPs and CeO_2NPs). The dynamic nature of nanomaterials in the environment makes the effective extraction from

environmental compartments (such as soil and sewage sludge) however a challenge. Moreover, many of the current extraction methods have the potential to modify NPs. Although the concentrations of some NPs in the environmental compartments were predicted with the help of mathematic modeling, these results need to be further validated with appropriate analytical techniques. Therefore, future research is needed to improve the methods for sample preparation and to extend more techniques to make them suited for the detection of NPs in the environment.

2) As stated in this thesis, the relative contribution of nanoparticulate and dissolved ions to the bioavailability of NPs is important to understanding the toxicity mechanism of NPs. Currently, the quantitative analysis of metallic NPs is usually focused on the metallic mass concentrations as quantified with the help of ICP-MS based techniques. In this thesis, we distinguished the relative contribution of particles and ions with the help of modeling based on the total metal concentration in plants exposed to NPs and on reference experiments with metal salts (referred to as dissolved ions). Directly determining the concentrations of the nanoparticulate form and the dissolved ions released from NPs in organisms is a great difficulty, as faced by environmental and analytical scientists. The sp-ICP-MS and stable isotope-based analytical techniques show great potential in this field. However, these approaches are still in their infancy in this field. Much more effort needs to be paid to optimizing the performance of these techniques and improving their sensitivity to measure NPs. Additionally, to use these two methods NPs need to be extracted first by digestion of the samples, which may modify the properties of the NPs. Similarly, NPs accumulated inside organisms may also undergo a series of dynamic transformations. Therefore, the development of new methods and techniques or the use of a combination of multiple techniques that will enable to quantify the *in-site* and real-time concentration of NPs in organisms is urgently needed.

3) In this thesis, we investigated the uptake and translocation of NP in plants and snails without considering their subcellular location and the potential speciation patterns inside organisms. Such information is very valuable for a better and comprehensive understanding of the internalization of NPs inside biota. Transmission electron microscopy, confocal laser scanning microscopy or

fluorescence microscopy have been used to track the subcellular location of dyed/labeled NPs in organisms. But there are important limitations to these methods, including detachment of dye/labels attached to the NPs, while some techniques are not suitable for undyed/labeled NPs. Microbeam X-ray fluorescence mapping (μ-XRF) and X-ray absorption near edge structure spectroscopy (μ-XANES) can be used to identify the chemical speciation of NPs in organisms. But the lateral resolution of most μ-XRF/μ-XAS beamlines in the world is above 1 μm or a few hundred nm[111]. The development of higher spatial resolution techniques is therefore needed to further advance our understanding of the subcellular fate of NPs in organisms.

6.3.2 NPs exposure

Even though the results presented in this thesis improve the understanding of the interactions of NPs with terrestrial biota to a certain extent and provide implications for risk assessment of NPs, there is still a long way to go to get a fully clear picture of nano-ecotoxicology. Therefore, based on the results of this thesis, I will propose several issues that deserve further investigation:

1) Although we conducted long-term experiments, the results reported in this thesis did not cover the full life cycle of plants and snails. As a result, we may underestimate or overestimate the impacts of NPs on biota. Also, the growth stages of the tested organisms play an important role in affecting the toxicity of NPs. Therefore, full life cycle studies of different plants and snails in response to NPs exposure are needed for future research, as this may give a more realistic evaluation of the real effects of NPs on biota.

2) We investigated the effects of the exposure pathway, the exposure concentration and time, and the physicochemical properties of NPs on their impacts. In addition, environmental conditions such as the pH, the NOM content, the ionic strength are also needed to be considered in assessing the environmental risks of NPs, and these properties are not specifically considered or modified in this thesis. In particular, we found that soil exposure of NPs to plants induced less toxicity compared to hydroponic exposure. The low bioavailability of metallic NPs in soil may be due to reduction of the transport of NPs, as affected by the characteristics of soil including

the pH, soil natural organic matter, the clay and mineral contents in soil, and the activity of soil microbes. To better understand the interactions between NPs and biota, further efforts should be devoted to studying how the environmental conditions influence the toxicity of NPs in plants and how soil components affect the behaviors of NPs in soil.

3) We confirmed the occurrence of mixture toxicity and trophic transfer of NPs along a simple two-trophic level food chain. The design of the experiments was focused on establishing and maintaining controlled conditions. In a natural ecosystem, the exposure conditions are more dynamic and transfer between organisms is likely to be more complex as well as due to the changing exposure conditions the bioavailable fraction of the NPs will change. Further mesocosm studies and even field research including more species and using environmentally relevant concentrations of NPs are therefore needed to properly simulate realistic exposure scenarios.

Sahara, Morocco, 2018

Photo by Yupeng

Björkliden, Kiruna, Sweden, 2019

References

1. Feynman, R. P. There's Plenty of Room at the Bottom. *Eng. Sci.* **23**, 22–36 (1959).
2. Rai, P. K. *et al.* Nanoparticle-plant interaction: Implications in energy, environment, and agriculture. *Environ. Int.* **119**, 1–19 (2018).
3. Taniguchi N.; Arakawa, C.; Kobayashi, T. On the Basic concept of Nanotechnology. *Proc. Int. Conf. Prod. Eng.* (1974).
4. Bayda, S., Adeel, M., Tuccinardi, T., Cordani, M. & Rizzolio, F. The History of Nanoscience and Nanotechnology: From Chemical–Physical Applications to Nanomedicine. *Mol. 2020, Vol. 25, Page 112* **25**, 112 (2019).
5. National Nanotechnology Initiative. What is nanotechnology? Available at: https://www.nano.gov/nanotechnology-facts. (Accessed: 28th July 2021)
6. Hannah, W. & Thompson, P. B. Nanotechnology, risk and the environment: a review. *J. Environ. Monit.* **10**, 291–300 (2008).
7. Lauterwasser, C. *Opportunities and risks of Nanotechnologies Report in co-operation with the OECD International Futures Programme.* (2014).
8. Danish Consumer Council. *The Nanodatabase.*
9. *Global Nanotechnology Market (by Component and Applications), Funding & Investment, Patent Analysis and 27 Companies Profile & Recent Developments - Forecast to 2024.*
10. Roco, M. C. Overview:Affirmation of Nanotechnology between 2000 and 2030. in *Nanotechnology Commercialization:Manufacturing Processes and Products* 1–23 (John Wiley & Sons, Inc., 2017). doi:10.1002/9781119371762.ch1
11. The European Commission. *Assessing the environmental safety of manufactured nanomaterials.* (2017). doi:10.2779/690478
12. Camboni, M., Hanlon, J., García, R. P. & Floyd, P. *A State of Play Study of the market for so called 'Next Generation' Nanomaterials. European Chemicals Agency* (2019). doi:10.2823/242422
13. Dolez, P. I. Nanomaterials Definitions, Classifications, and Applications. in *Nanoengineering: Global Approaches to Health and Safety Issues* 3–40 (Elsevier, 2015). doi:10.1016/B978-0-444-62747-6.00001-4
14. Abbas, Q. *et al.* Environmental transformation and nano-toxicity of engineered nano-particles (ENPs) in aquatic and terrestrial organisms. *Crit. Rev. Environ. Sci. Technol.* **50**, 2523–2581 (2020).
15. Usman, M. *et al.* Nanotechnology in agriculture: Current status, challenges and future opportunities. *Science of the Total Environment* **721**, 137778 (2020).
16. Wang, Z., Zhang, L., Zhao, J. & Xing, B. Environmental processes and toxicity of metallic nanoparticles in aquatic systems as affected by natural organic matter. *Environmental Science: Nano* **3**, 240–255 (2016).
17. Tourinho, P. S. *et al.* Metal-based nanoparticles in soil: Fate, behavior, and

effects on soil invertebrates. *Environmental Toxicology and Chemistry* **31**, 1679–1692 (2012).

18. Piccinno, F., Gottschalk, F., Seeger, S. & Nowack, B. Industrial production quantities and uses of ten engineered nanomaterials in Europe and the world. *Journal of Nanoparticle Research* **14**, 1–11 (2012).
19. Keller, A. A. & Lazareva, A. Predicted Releases of Engineered Nanomaterials: From Global to Regional to Local. *Environ. Sci. Technol. Lett.* **1**, 65–70 (2013).
20. Pulit-Prociak, J. & Banach, M. Silver nanoparticles - A material of the future...? *Open Chem.* **14**, 76–91 (2016).
21. Singh, H. *et al.* Recent advances in the applications of nano-agrochemicals for sustainable agricultural development. *Environ. Sci. Process. Impacts* **23**, 213–239 (2021).
22. Kahru, A. & Dubourguier, H. C. From ecotoxicology to nanoecotoxicology. *Toxicology* **269**, 105–119 (2010).
23. Oberdörster, G. *et al.* Principles for characterizing the potential human health effects from exposure to nanomaterials: Elements of a screening strategy. *Particle and Fibre Toxicology* **2**, 1–35 (2005).
24. Abbas, Q. *et al.* Transformation pathways and fate of engineered nanoparticles (ENPs) in distinct interactive environmental compartments: A review. *Environment International* **138**, 105646 (2020).
25. Barros, D. *et al.* Proteomics and antioxidant enzymes reveal different mechanisms of toxicity induced by ionic and nanoparticulate silver in bacteria. *Environ. Sci. Nano* **6**, 1207–1218 (2019).
26. Zhai, Y. *et al.* Compositional and predicted functional dynamics of soil bacterial community in response to single pulse and repeated dosing of titanium dioxide nanoparticles. *NanoImpact* **16**, 100187 (2019).
27. Liu, H. *et al.* Toxicity responses of different organs of zebrafish (Danio rerio) to silver nanoparticles with different particle sizes and surface coatings. *Environ. Pollut.* 414–422 (2019). doi:10.1016/j.envpol.2018.12.034
28. Ye, N., Wang, Z., Wang, S. & Peijnenburg, W. J. G. M. Toxicity of mixtures of zinc oxide and graphene oxide nanoparticles to aquatic organisms of different trophic level: particles outperform dissolved ions. *Nanotoxicology* **12**, 423–438 (2018).
29. Navarro, E., Wagner, B., Odzak, N., Sigg, L. & Behra, R. Effects of Differently Coated Silver Nanoparticles on the Photosynthesis of Chlamydomonas reinhardtii. *Environ. Sci. Technol.* **49**, 8041–8047 (2015).
30. Kwak, J. Il & An, Y. J. The current state of the art in research on engineered nanomaterials and terrestrial environments: Different-scale approaches. *Environmental Research* **151**, 368–382 (2016).
31. Geitner, N. K. *et al.* Size-Based Differential Transport, Uptake, and Mass Distribution of Ceria (CeO2) Nanoparticles in Wetland Mesocosms. *Environ. Sci. Technol.* **52**, 9768–9776 (2018).

32. The risks of nanomaterial risk assessment. *Nature Nanotechnology* **15**, 163 (2020).

33. Bundschuh, M. *et al.* Nanoparticles in the environment: where do we come from, where do we go to? *Environmental Sciences Europe* **30**, 6 (2018).

34. Gardea-Torresdey, J. L., Rico, C. M. & White, J. C. Trophic transfer, transformation, and impact of engineered nanomaterials in terrestrial environments. *Environ. Sci. Technol.* **48**, 2526–2540 (2014).

35. Yan, A. & Chen, Z. Impacts of silver nanoparticles on plants: A focus on the phytotoxicity and underlying mechanism. *International Journal of Molecular Sciences* **20**, 1003 (2019).

36. Gunawan, C., Lim, M., Marquis, C. P. & Amal, R. Nanoparticle-protein corona complexes govern the biological fates and functions of nanoparticles. *J. Mater. Chem. B* **2**, 2060–2083 (2014).

37. Lynch, I. & Dawson, K. A. Protein-nanoparticle interactions. *Nano Today* **3**, 40–47 (2008).

38. Ivask, A. *et al.* Mechanisms of toxic action of Ag, ZnO and CuO nanoparticles to selected ecotoxicological test organisms and mammalian cells in vitro : A comparative review. *Nanotoxicology* **8**, 57–71 (2014).

39. Escorihuela, L., Martorell, B., Rallo, R. & Fernández, A. Toward computational and experimental characterisation for risk assessment of metal oxide nanoparticles. *Environmental Science: Nano* **5**, 2241–2251 (2018).

40. Hristozov, D. *et al.* Frameworks and tools for risk assessment of manufactured nanomaterials. *Environment International* **95**, 36–53 (2016).

41. Wiesner, M. R., Lowry, G. V., Alvarez, P., Dionysiou, D. & Biswas, P. Assessing the risks of manufactured nanomaterials. *Environmental Science and Technology* **40**, 4336–4345 (2006).

42. Gottschalk, F. & Nowack, B. The release of engineered nanomaterials to the environment. *J. Environ. Monit.* **13**, 1145–1155 (2011).

43. Mueller, N. C. & Nowack, B. Exposure modeling of engineered nanoparticles in the environment. *Environ. Sci. Technol.* **42**, 4447–4453 (2008).

44. Nowack, B. *et al.* The Flows of Engineered Nanomaterials from Production, Use, and Disposal to the Environment. in *Handbook of Environmental Chemistry* **48**, 209–231 (Springer, Cham, 2016).

45. Keller, A. A., McFerran, S., Lazareva, A. & Suh, S. Global life cycle releases of engineered nanomaterials. *J. Nanoparticle Res.* **15**, 1–17 (2013).

46. Fajardo, C. *et al.* Assessing the impact of zero-valent iron (ZVI) nanotechnology on soil microbial structure and functionality: A molecular approach. *Chemosphere* **86**, 802–808 (2012).

47. Servin, A. D. & White, J. C. Nanotechnology in agriculture: Next steps for understanding engineered nanoparticle exposure and risk. *NanoImpact* **1**, 9–12 (2016).

48. Chhipa, H. Nanofertilizers and nanopesticides for agriculture. *Environmental*

Chemistry Letters **15**, 15–22 (2017).

49. Del Real, A. E. P. *et al.* Fate of Ag-NPs in Sewage Sludge after Application on Agricultural Soils. *Environ. Sci. Technol.* **50**, 1759–1768 (2016).

50. Pan, B. & Xing, B. Applications and implications of manufactured nanoparticles in soils: a review. *Eur. J. Soil Sci.* **63**, 437–456 (2012).

51. Zhao, J., Lin, M., Wang, Z., Cao, X. & Xing, B. Engineered nanomaterials in the environment: Are they safe? *Critical Reviews in Environmental Science and Technology* **51**, 1443–1478 (2021).

52. Sun, T. Y., Gottschalk, F., Hungerbühler, K. & Nowack, B. Comprehensive probabilistic modelling of environmental emissions of engineered nanomaterials. *Environ. Pollut.* **185**, 69–76 (2014).

53. Amde, M., Liu, J. fu, Tan, Z. Q. & Bekana, D. Transformation and bioavailability of metal oxide nanoparticles in aquatic and terrestrial environments. A review. *Environmental Pollution* **230**, 250–267 (2017).

54. Kaegi, R. *et al.* Fate and transformation of silver nanoparticles in urban wastewater systems. *Water Res.* **47**, 3866–3877 (2013).

55. Tan, W., Peralta-Videa, J. R. & Gardea-Torresdey, J. L. Interaction of titanium dioxide nanoparticles with soil components and plants: Current knowledge and future research needs-a critical review. *Environmental Science: Nano* **5**, 257–278 (2018).

56. Pokhrel, L. R. & Dubey, B. Evaluation of developmental responses of two crop plants exposed to silver and zinc oxide nanoparticles. *Sci. Total Environ.* **452–453**, 321–332 (2013).

57. Zhang, L. & Wang, W. X. Dominant Role of Silver Ions in Silver Nanoparticle Toxicity to a Unicellular Alga: Evidence from Luminogen Imaging. *Environ. Sci. Technol.* **53**, 494–502 (2019).

58. Li, X. *et al.* Silver nanoparticle toxicity and association with the alga Euglena gracilis. *Environ. Sci. Nano* **2**, 594–602 (2015).

59. Visnapuu, M. *et al.* Dissolution of silver nanowires and nanospheres dictates their toxicity to escherichia coli. *Biomed Res. Int.* **2013**, (2013).

60. Zhang, Z. *et al.* Impact of copper nanoparticles and ionic copper exposure on wheat (Triticum aestivum L.) root morphology and antioxidant response. *Environ. Pollut.* **239**, 689–697 (2018).

61. Yin, L. *et al.* More than the ions: The effects of silver nanoparticles on lolium multiflorum. *Environ. Sci. Technol.* **45**, 2360–2367 (2011).

62. Yang, X., Pan, H., Wang, P. & Zhao, F. J. Particle-specific toxicity and bioavailability of cerium oxide (CeO2) nanoparticles to Arabidopsis thaliana. *J. Hazard. Mater.* **322**, 292–300 (2017).

63. Ko, K.-S., Koh, D.-C. & Kong, I. C. Toxicity Evaluation of Individual and Mixtures of Nanoparticles Based on Algal Chlorophyll Content and Cell Count. *Mater. 2018, Vol. 11, Page 121* **11**, 121 (2018).

64. Albanese, A. & Chan, W. C. W. Effect of gold nanoparticle aggregation on cell

uptake and toxicity. in *ACS Nano* **5**, 5478–5489 (American Chemical Society, 2011).

65. Cho, E. C., Zhang, Q. & Xia, Y. The effect of sedimentation and diffusion on cellular uptake of gold nanoparticles. *Nat. Nanotechnol.* **6**, 385–391 (2011).

66. Pauluhn, J. Pulmonary toxicity and fate of agglomerated 10 and 40 nm aluminum oxyhydroxides following 4-week inhalation exposure of rats: Toxic effects are determined by agglomerated, not primary particle size. *Toxicol. Sci.* **109**, 152–167 (2009).

67. Soto, K., Garza, K. M. & Murr, L. E. Cytotoxic effects of aggregated nanomaterials. *Acta Biomater.* **3**, 351–358 (2007).

68. Schwab, F. *et al.* Barriers, pathways and processes for uptake, translocation and accumulation of nanomaterials in plants – Critical review. *Nanotoxicology* **10**, 1–22 (2015).

69. Lv, J., Christie, P. & Zhang, S. Uptake, translocation, and transformation of metal-based nanoparticles in plants: recent advances and methodological challenges. *Environ. Sci. Nano* **6**, 41–59 (2019).

70. Sabo-Attwood, T. *et al.* Uptake, distribution and toxicity of gold nanoparticles in tobacco (Nicotiana xanthi) seedlings. *Nanotoxicology* **6**, 353–360 (2012).

71. Cvjetko, P. *et al.* Toxicity of silver ions and differently coated silver nanoparticles in Allium cepa roots. *Ecotoxicol. Environ. Saf.* **137**, 18–28 (2017).

72. Jiang, H. S., Qiu, X. N., Li, G. B., Li, W. & Yin, L. Y. Silver nanoparticles induced accumulation of reactive oxygen species and alteration of antioxidant systems in the aquatic plant Spirodela polyrhiza. *Environ. Toxicol. Chem.* **33**, 1398–1405 (2014).

73. Syu, Y. yu, Hung, J. H., Chen, J. C. & Chuang, H. wen. Impacts of size and shape of silver nanoparticles on Arabidopsis plant growth and gene expression. *Plant Physiol. Biochem.* **83**, 57–64 (2014).

74. Pedruzzi, D. P. *et al.* ZnO nanoparticles impact on the photosynthetic activity of Vicia faba: Effect of particle size and concentration. *NanoImpact* **19**, 100246 (2020).

75. Lv, Z. *et al.* Interaction of different-sized ZnO nanoparticles with maize (Zea mays): Accumulation, biotransformation and phytotoxicity. *Sci. Total Environ.* **796**, 148927 (2021).

76. Xiang, L. *et al.* Effects of the size and morphology of zinc oxide nanoparticles on the germination of Chinese cabbage seeds. *Environ. Sci. Pollut. Res.* **22**, 10452–10462 (2015).

77. Yusefi-Tanha, E., Fallah, S., Rostamnejadi, A. & Pokhrel, L. R. Particle size and concentration dependent toxicity of copper oxide nanoparticles (CuONPs) on seed yield and antioxidant defense system in soil grown soybean (Glycine max cv. Kowsar). *Sci. Total Environ.* **715**, 136994 (2020).

78. Gubbins, E. J., Batty, L. C. & Lead, J. R. Phytotoxicity of silver nanoparticles to Lemna minor L. *Environ. Pollut.* **159**, 1551–1559 (2011).

79. Thuesombat, P., Hannongbua, S., Akasit, S. & Chadchawan, S. Effect of silver nanoparticles on rice (Oryza sativa L. cv. KDML 105) seed germination and seedling growth. *Ecotoxicol. Environ. Saf.* **104**, 302–309 (2014).

80. Demir, E., Kaya, N. & Kaya, B. Genotoxic effects of zinc oxide and titanium dioxide nanoparticles on root meristem cells of allium cepa by comet assay. *Turkish J. Biol.* **38**, 31–39 (2014).

81. Majumdar, S. *et al.* Surface coating determines the response of soybean plants to cadmium sulfide quantum dots. *NanoImpact* **14**, 100151 (2019).

82. Torrent, L. *et al.* Uptake, translocation and ligand of silver in Lactuca sativa exposed to silver nanoparticles of different size, coatings and concentration. *J. Hazard. Mater.* **384**, 121201 (2020).

83. Perreault, F., Popovic, R. & Dewez, D. Different toxicity mechanisms between bare and polymer-coated copper oxide nanoparticles in Lemna gibba. *Environ. Pollut.* **185**, 219–227 (2014).

84. Zhang, P. *et al.* Shape-dependent transformation and translocation of ceria nanoparticles in cucumber plants. *Environ. Sci. Technol. Lett.* **4**, 380–385 (2017).

85. Gorka, D. E. & Liu, J. Effect of Direct Contact on the Phytotoxicity of Silver Nanomaterials. *Environ. Sci. Technol.* **50**, 10370–10376 (2016).

86. Gorka, D. E. *et al.* Reducing Environmental Toxicity of Silver Nanoparticles through Shape Control. *Environ. Sci. Technol.* **49**, 10093–10098 (2015).

87. Sohn, E. K. *et al.* Aquatic Toxicity Comparison of Silver Nanoparticles and Silver Nanowires. *Biomed Res. Int.* **2015**, 1–12 (2015).

88. Abdolahpur Monikh, F. *et al.* Do the joint effects of size, shape and ecocorona influence the attachment and physical eco(cyto)toxicity of nanoparticles to algae? *Nanotoxicology* **14**, 310–325 (2020).

89. Nam, S. H. & An, Y. J. Size- and shape-dependent toxicity of silver nanomaterials in green alga Chlorococcum infusionum. *Ecotoxicol. Environ. Saf.* **168**, 388–393 (2019).

90. Wang, P. *et al.* Silver sulfide nanoparticles (Ag2S-NPs) are taken up by plants and are phytotoxic. *Nanotoxicology* **9**, 1041–1049 (2015).

91. Zhai, Y. *et al.* Compositional alterations in soil bacterial communities exposed to TiO2 nanoparticles are not reflected in functional impacts. *Environ. Res.* **178**, 108713 (2019).

92. Stampoulis, D., Sinha, S. K. & White, J. C. Assay-dependent phytotoxicity of nanoparticles to plants. *Environ. Sci. Technol.* **43**, 9473–9479 (2009).

93. Jośko, I. *et al.* Long-term effect of ZnO and CuO nanoparticles on soil microbial community in different types of soil. *Geoderma* **352**, 204–212 (2019).

94. Dai, Y. *et al.* Interaction of CuO nanoparticles with plant cells: Internalization, oxidative stress, electron transport chain disruption, and toxicogenomic responses. *Environ. Sci. Nano* **5**, 2269–2281 (2018).

95. da Cruz, T. N. M. *et al.* A new glance on root-to-shoot in vivo zinc transport and time-dependent physiological effects of ZnSO4 and ZnO nanoparticles on plants. *Sci. Rep.* **9**, (2019).

96. Chen, X., O'Halloran, J. & Jansen, M. A. K. Time Matters: the Toxicity of Zinc Oxide Nanoparticles to Lemna minor L. Increases with Exposure Time. *Water. Air. Soil Pollut.* **229**, 1–10 (2018).

97. Aravantinou, A. F., Andreou, F. & Manariotis, I. D. Long-term toxicity of ZnO nanoparticles to Scenedesmus rubescens cultivated in different media. *Sci. Rep.* **7**, 1–11 (2017).

98. Schlich, K. *et al.* Long-term effects of three different silver sulfide nanomaterials, silver nitrate and bulk silver sulfide on soil microorganisms and plants. *Environ. Pollut.* **242**, 1850–1859 (2018).

99. Jeyasubramanian, K. *et al.* Enhancement in growth rate and productivity of spinach grown in hydroponics with iron oxide nanoparticles. *RSC Adv.* **6**, 15451–15459 (2016).

100. Deng, R. *et al.* Nanoparticle interactions with co-existing contaminants: joint toxicity, bioaccumulation and risk. *Nanotoxicology* **11**, 591–612 (2017).

101. Yu, R. *et al.* Toxicity of binary mixtures of metal oxide nanoparticles to Nitrosomonas europaea. *Chemosphere* **153**, 187–197 (2016).

102. Tong, T. *et al.* Combined Toxicity of Nano-ZnO and Nano-TiO2: From Single- to Multinanomaterial Systems. *Environ. Sci. Technol.* **49**, 8113–8123 (2015).

103. Tong, T. *et al.* Chemical interactions between nano-ZnO and nano-TiO2 in a natural aqueous medium. *Environ. Sci. Technol.* **48**, 7924–7932 (2014).

104. Huynh, K. A., McCaffery, J. M. & Chen, K. L. Heteroaggregation Reduces Antimicrobial Activity of Silver Nanoparticles: Evidence for Nanoparticle–Cell Proximity Effects. *Environ. Sci. Technol. Lett.* **1**, 361–366 (2014).

105. Jośko, I., Oleszczuk, P. & Skwarek, E. Toxicity of combined mixtures of nanoparticles to plants. *J. Hazard. Mater.* **331**, 200–209 (2017).

106. Singh, D. & Kumar, A. Impact of Irrigation Using Water Containing CuO and ZnO Nanoparticles on Spinach oleracea Grown in Soil Media. *Bull. Environ. Contam. Toxicol. 2016 974* **97**, 548–553 (2016).

107. Wang, Y., Cai, R. & Chen, C. The Nano–Bio Interactions of Nanomedicines: Understanding the Biochemical Driving Forces and Redox Reactions. *Acc. Chem. Res.* **52**, 1507–1518 (2019).

108. Qu, G. *et al.* Property-Activity Relationship of Black Phosphorus at the Nano-Bio Interface: From Molecules to Organisms. *Chemical Reviews* **120**, 2288–2346 (2020).

109. Ma, Y. *et al.* Phytotoxicity and biotransformation of La 2O 3 nanoparticles in a terrestrial plant cucumber (Cucumis sativus). *Nanotoxicology* **5**, 743–753 (2011).

110. Geisler-Lee, J. *et al.* Phytotoxicity, accumulation and transport of silver

nanoparticles by Arabidopsis thaliana. *Nanotoxicology* **7**, 323–337 (2013).

111. Lv, J., Christie, P. & Zhang, S. Uptake, translocation, and transformation of metal-based nanoparticles in plants: recent advances and methodological challenges. *Environmental Science: Nano* **6**, 41–59 (2019).

112. Nair, R. *et al.* Nanoparticulate material delivery to plants. *Plant Science* **179**, 154–163 (2010).

113. Li, L. *et al.* Effective uptake of submicrometre plastics by crop plants via a crack-entry mode. *Nat. Sustain.* **3**, 929–937 (2020).

114. Tripathi, D. K. *et al.* Uptake, Accumulation and Toxicity of Silver Nanoparticle in Autotrophic Plants, and Heterotrophic Microbes: A Concentric Review. *Front. Microbiol.* **08**, 7 (2017).

115. Judy, J. D. & Bertsch, P. M. Bioavailability, Toxicity, and Fate of Manufactured Nanomaterials in Terrestrial Ecosystems. in *Advances in Agronomy* **123**, 1–64 (Academic Press Inc., 2014).

116. Peng, C. *et al.* Bioavailability and translocation of metal oxide nanoparticles in the soil-rice plant system. *Sci. Total Environ.* **713**, 136662 (2020).

117. Zhang, Z. *et al.* Uptake and distribution of ceria nanoparticles in cucumber plants. *Metallomics* **3**, 816–822 (2011).

118. Salehi, H., Chehregani, A., Lucini, L., Majd, A. & Gholami, M. Morphological, proteomic and metabolomic insight into the effect of cerium dioxide nanoparticles to Phaseolus vulgaris L. under soil or foliar application. *Science of the Total Environment* **616–617**, 1540–1551 (2018).

119. Tripathi, D. K. *et al.* An overview on manufactured nanoparticles in plants: Uptake, translocation, accumulation and phytotoxicity. *Plant Physiology and Biochemistry* **110**, 2–12 (2017).

120. Liu, W. *et al.* Interactions of metal-based nanoparticles (Mbnps) and metal-oxide nanoparticles (monps) with crop plants: A critical review of research progress and prospects. *Environmental Reviews* **28**, 294–310 (2020).

121. Ghosh, M., Bandyopadhyay, M. & Mukherjee, A. Genotoxicity of titanium dioxide (TiO2) nanoparticles at two trophic levels: Plant and human lymphocytes. *Chemosphere* **81**, 1253–1262 (2010).

122. Ghosh, M., Ghosh, I., Godderis, L., Hoet, P. & Mukherjee, A. Genotoxicity of engineered nanoparticles in higher plants. *Mutation Research - Genetic Toxicology and Environmental Mutagenesis* **842**, 132–145 (2019).

123. Zhu, Y. *et al.* Nanomaterials and plants: Positive effects, toxicity and the remediation of metal and metalloid pollution in soil. *Sci. Total Environ.* **662**, 414–421 (2019).

124. Kaveh, R. *et al.* Changes in Arabidopsis thaliana gene expression in response to silver nanoparticles and silver ions. *Environ. Sci. Technol.* **47**, 10637–10644 (2013).

125. Rastogi, A. *et al.* Impact of Metal and Metal Oxide Nanoparticles on Plant: A Critical Review. *Front. Chem.* **5**, 78 (2017).

126. Milani, N. *et al.* Dissolution kinetics of macronutrient fertilizers coated with manufactured zinc oxide nanoparticles. *J. Agric. Food Chem.* **60**, 3991–3998 (2012).

127. Gogos, A., Knauer, K. & Bucheli, T. D. Nanomaterials in plant protection and fertilization: Current state, foreseen applications, and research priorities. *J. Agric. Food Chem.* **60**, 9781–9792 (2012).

128. Yuvaraj, M. & Subramanian, K. S. Controlled-release fertilizer of zinc encapsulated by a manganese hollow core shell. *Soil Sci. Plant Nutr.* **61**, 319–326 (2014).

129. Avellan, A. *et al.* Nanoparticle Size and Coating Chemistry Control Foliar Uptake Pathways, Translocation, and Leaf-to-Rhizosphere Transport in Wheat. *ACS Nano* **13**, 5291–5305 (2019).

130. Song, U. *et al.* Functional analyses of nanoparticle toxicity: A comparative study of the effects of TiO2 and Ag on tomatoes (Lycopersicon esculentum). *Ecotoxicol. Environ. Saf.* **93**, 60–67 (2013).

131. Chavalmane, S. *et al.* Mechanistic evaluation of translocation and physiological impact of titanium dioxide and zinc oxide nanoparticles on the tomato (Solanum lycopersicum L.) plant. *Metallomics* **7**, 1584–1594 (2015).

132. Ameen, F., Alsamhary, K., Alabdullatif, J. A. & ALNadhari, S. A review on metal-based nanoparticles and their toxicity to beneficial soil bacteria and fungi. *Ecotoxicol. Environ. Saf.* **213**, 112027 (2021).

133. Lewis, R. W., Bertsch, P. M. & McNear, D. H. Nanotoxicity of engineered nanomaterials (ENMs) to environmentally relevant beneficial soil bacteria – a critical review. *Nanotoxicology* **13**, 392–428 (2019).

134. Xu, C. *et al.* Distinctive effects of TiO2 and CuO nanoparticles on soil microbes and their community structures in flooded paddy soil. *Soil Biol. Biochem.* **86**, 24–33 (2015).

135. Simonin, M. & Richaume, A. Impact of engineered nanoparticles on the activity, abundance, and diversity of soil microbial communities: a review. *Environ. Sci. Pollut. Res. 2015 2218* **22**, 13710–13723 (2015).

136. Zhai, Y., Hunting, E. R., Wouters, M., Peijnenburg, W. J. G. M. & Vijver, M. G. Silver Nanoparticles, Ions, and Shape Governing Soil Microbial Functional Diversity: Nano Shapes Micro. *Front. Microbiol.* **7**, (2016).

137. Samarajeewa, A. D. *et al.* Effect of silver nano-particles on soil microbial growth, activity and community diversity in a sandy loam soil. *Environ. Pollut.* **220**, 504–513 (2017).

138. Zhang, X. *et al.* Assessing the Impacts of Cu(OH)2 Nanopesticide and Ionic Copper on the Soil Enzyme Activity and Bacterial Community. *ACS Appl. Mater. Interfaces* **68**, 3381 (2020).

139. Meier, M. J., Dodge, A. E., Samarajeewa, A. D. & Beaudette, L. A. Soil exposed to silver nanoparticles reveals significant changes in community structure and altered microbial transcriptional profiles. *Environ. Pollut.* **258**, 113816 (2020).

140. Philippot, L., Raaijmakers, J. M., Lemanceau, P. & Van Der Putten, W. H.

Going back to the roots: The microbial ecology of the rhizosphere. *Nature Reviews Microbiology* **11**, 789–799 (2013).

141. Zhang, R., Vivanco, J. M. & Shen, Q. The unseen rhizosphere root–soil–microbe interactions for crop production. *Current Opinion in Microbiology* **37**, 8–14 (2017).

142. Zhao, L. *et al.* Metabolomics reveals that engineered nanomaterial exposure in soil alters both soil rhizosphere metabolite profiles and maize metabolic pathways. *Environ. Sci. Nano* **6**, 1716–1727 (2019).

143. Zhao, M. *et al.* Root exudates drive soil-microbe-nutrient feedbacks in response to plant growth. *Plant Cell Environ.* **44**, 613–628 (2021).

144. Esitken, A. *et al.* Effects of plant growth promoting bacteria (PGPB) on yield, growth and nutrient contents of organically grown strawberry. *Sci. Hortic. (Amsterdam).* **124**, 62–66 (2010).

145. Dai, Y. *et al.* Uptake, Transport, and Transformation of CeO 2 Nanoparticles by Strawberry and Their Impact on the Rhizosphere Bacterial Community. *ACS Sustain. Chem. Eng. Eng.* **8**, 4792–4800 (2020).

146. Guan, X. *et al.* CuO Nanoparticles Alter the Rhizospheric Bacterial Community and Local Nitrogen Cycling for Wheat Grown in a Calcareous Soil. *Environ. Sci. Technol.* **54**, 8699–8709 (2020).

147. Avellan, A. *et al.* Critical Review: Role of Inorganic Nanoparticle Properties on Their Foliar Uptake and in Planta Translocation. *Environ. Sci. Technol.* (2021). doi:10.1021/acs.est.1c00178

148. Kibbey, T. C. G. & Strevett, K. A. The effect of nanoparticles on soil and rhizosphere bacteria and plant growth in lettuce seedlings. *Chemosphere* **221**, 703–707 (2019).

149. Sillen, W. M. A. *et al.* Effects of silver nanoparticles on soil microorganisms and maize biomass are linked in the rhizosphere. *Soil Biol. Biochem.* **91**, 14–22 (2015).

150. Caixeta, M. B. *et al.* Toxicity of engineered nanomaterials to aquatic and land snails: A scientometric and systematic review. *Chemosphere* **260**, 127654 (2020).

151. De Vaufleury, A. *et al.* How terrestrial snails can be used in risk assessment of soils. in *Environmental Toxicology and Chemistry* **25**, 797–806 (2006).

152. Baroudi, F., Al Alam, J., Fajloun, Z. & Millet, M. Snail as sentinel organism for monitoring the environmental pollution; a review. *Ecological Indicators* **113**, 106240 (2020).

153. Starnes, D. L. *et al.* Impact of sulfidation on the bioavailability and toxicity of silver nanoparticles to Caenorhabditis elegans. *Environ. Pollut.* **196**, 239–246 (2015).

154. Quadros, M. E. *et al.* Release of Silver from Nanotechnology-Based Consumer Products for Children. *Environ. Sci. Technol.* **47**, 8894–8901 (2013).

155. Benn, T., Cavanagh, B., Hristovski, K., Posner, J. D. & Westerhoff, P. The

release of nanosilver from consumer products used in the home. *J. Environ. Qual.* **39**, 1875–1882 (2010).

156. Yu, S. J., Yin, Y. G. & Liu, J. F. Silver nanoparticles in the environment. *Environmental Sciences: Processes and Impacts* **15**, 78–92 (2013).

157. Wang, P. *et al.* Silver Nanoparticles Entering Soils via the Wastewater-Sludge-Soil Pathway Pose Low Risk to Plants but Elevated Cl Concentrations Increase Ag Bioavailability. *Environ. Sci. Technol.* **50**, 8274–8281 (2016).

158. Li, M., Wang, P., Dang, F. & Zhou, D. M. The transformation and fate of silver nanoparticles in paddy soil: effects of soil organic matter and redox conditions. *Environ. Sci. Nano* **4**, 919–928 (2017).

159. Park, J. *et al.* Characterization of exposure to silver nanoparticles in a manufacturing facility. *J. Nanoparticle Res.* **11**, 1705–1712 (2009).

160. Holder, A. L. & Marr, L. C. Toxicity of silver nanoparticles at the air-liquid interface. *Biomed Res. Int.* **2013**, 328934 (2013).

161. Li, C.-C. C. *et al.* Effects of exposure pathways on the accumulation and phytotoxicity of silver nanoparticles in soybean and rice. *Nanotoxicology* **11**, 699–709 (2017).

162. Lian, J. *et al.* Foliar spray of TiO2 nanoparticles prevails over root application in reducing Cd accumulation and mitigating Cd-induced phytotoxicity in maize (Zea mays L.). *Chemosphere* **239**, 124794 (2020).

163. Navarro, E. *et al.* Toxicity of silver nanoparticles to Chlamydomonas reinhardtii. *Environ. Sci. Technol.* **42**, 8959–8964 (2008).

164. Tripathi, A. *et al.* Differential phytotoxic responses of silver nitrate (AgNO3) and silver nanoparticle (AgNps) in Cucumis sativus L. *Plant Gene* **11**, 255–264 (2017).

165. Li, X. *et al.* Silver nanoparticle toxicity and association with the alga Euglena gracilis. *Environ. Sci. Nano* **2**, 594–602 (2015).

166. Qian, H. *et al.* Comparison of the toxicity of silver nanoparticles and silver ions on the growth of terrestrial plant model Arabidopsis thaliana. *J. Environ. Sci. (China)* **25**, 1947–1956 (2013).

167. Raliya, R. *et al.* Quantitative Understanding of Nanoparticle Uptake in Watermelon Plants. *Frontiers in Plant Science* **7**, (2016).

168. Wang, W. N., Tarafdar, J. C. & Biswas, P. Nanoparticle synthesis and delivery by an aerosol route for watermelon plant foliar uptake. *J. Nanoparticle Res.* **15**, (2013).

169. Achari, G. A. & Kowshik, M. Recent Developments on Nanotechnology in Agriculture: Plant Mineral Nutrition, Health, and Interactions with Soil Microflora. *Journal of Agricultural and Food Chemistry* **66**, 8647–8661 (2018).

170. Poynton, H. C. *et al.* Differential gene expression in daphnia magna suggests distinct modes of action and bioavailability for Zno nanoparticles and Zn ions. *Environ. Sci. Technol.* **45**, 762–768 (2011).

171. Xiao, Y., Vijver, M. G. & Peijnenburg, W. J. G. M. Impact of water chemistry

on the behavior and fate of copper nanoparticles. *Environ. Pollut.* **234**, 684–691 (2018).

172. Arenas-Lago, D., Abdolahpur Monikh, F., Vijver, M. G. & Peijnenburg, W. J. G. M. Dissolution and aggregation kinetics of zero valent copper nanoparticles in (simulated) natural surface waters: Simultaneous effects of pH, NOM and ionic strength. *Chemosphere* **226**, 841–850 (2019).

173. Jiang, H. S. *et al.* Silver nanoparticles induced reactive oxygen species via photosynthetic energy transport imbalance in an aquatic plant. *Nanotoxicology* **11**, 157–167 (2017).

174. Ma, C. *et al.* Defense mechanisms and nutrient displacement in: Arabidopsis thaliana upon exposure to CeO2 and In2O3 nanoparticles. *Environ. Sci. Nano* **3**, 1369–1379 (2016).

175. Lichtenthaler, H. K. Chlorophylls and Carotenoids: Pigments of Photosynthetic Biomembranes. *Methods Enzymol.* **148**, 350–382 (1987).

176. Wang, A. & Luo, G. Quanititative relation between the reaction of hydroxylamine and superoxide anion radicals in plants. *Plant Physiol Commun* **6**, 55-57 (in Chinese) (1990).

177. Mosa, K. A. *et al.* Copper Nanoparticles Induced Genotoxicty, Oxidative Stress, and Changes in Superoxide Dismutase (SOD) Gene Expression in Cucumber (Cucumis sativus) Plants. *Front. Plant Sci.* **9**, (2018).

178. Kampfenkel, K., Van Montagu, M. & Inzé, D. Extraction and determination of ascorbate and dehydroascorbate from plant tissue. *Anal. Biochem.* **225**, 165–167 (1995).

179. Xia, Z., Xu, Z., Wei, Y. & Wang, M. Overexpression of the Maize Sulfite Oxidase Increases Sulfate and GSH Levels and Enhances Drought Tolerance in Transgenic Tobacco. *Front. Plant Sci.* **9**, (2018).

180. Liu, Y., Baas, J., Peijnenburg, W. J. G. M. & Vijver, M. G. Evaluating the Combined Toxicity of Cu and ZnO Nanoparticles: Utility of the Concept of Additivity and a Nested Experimental Design. *Environ. Sci. Technol.* **50**, 5328–5337 (2016).

181. Nanotechnology - Project on Emerging Nanotechnologies. Available at: http://www.nanotechproject.org/. (Accessed: 22nd July 2019)

182. Vance, M. E. *et al.* Nanotechnology in the real world: Redeveloping the nanomaterial consumer products inventory. *Beilstein J. Nanotechnol.* **6**, 1769–1780 (2015).

183. Song, L., Vijver, M. G. & Peijnenburg, W. J. G. M. Comparative toxicity of copper nanoparticles across three Lemnaceae species. *Sci. Total Environ.* **518–519**, 217–224 (2015).

184. Stegemeier, J. P. *et al.* Speciation Matters: Bioavailability of Silver and Silver Sulfide Nanoparticles to Alfalfa (Medicago sativa). *Environ. Sci. Technol.* **49**, 8451–8460 (2015).

185. Piccapietra, F., Allué, C. G., Sigg, L. & Behra, R. Intracellular silver accumulation in Chlamydomonas reinhardtii upon exposure to carbonate

coated silver nanoparticles and silver nitrate. *Environ. Sci. Technol.* **46**, 7390–7397 (2012).

186. Stegemeier, J. P., Colman, B. P., Schwab, F., Wiesner, M. R. & Lowry, G. V. Uptake and Distribution of Silver in the Aquatic Plant Landoltia punctata (Duckweed) Exposed to Silver and Silver Sulfide Nanoparticles. *Environ. Sci. Technol.* **51**, 4936–4943 (2017).
187. Yang, Q. *et al.* Uptake and Transformation of Silver Nanoparticles and Ions by Rice Plants Revealed by Dual Stable Isotope Tracing. *Environ. Sci. Technol.* **53**, 625–633 (2019).
188. Peng, X., Palma, S., Fisher, N. S. & Wong, S. S. Effect of morphology of ZnO nanostructures on their toxicity to marine algae. *Aquat. Toxicol.* **102**, 186–196 (2011).
189. Geisler-Lee, J. *et al.* Reproductive Toxicity and Life History Study of Silver Nanoparticle Effect, Uptake and Transport in Arabidopsis thaliana. *Nanomaterials* **4**, 301–318 (2014).
190. Wang, P. *et al.* Characterizing the uptake, accumulation and toxicity of silver sulfide nanoparticles in plants. *Environ. Sci. Nano* **4**, 448–460 (2017).
191. Silva, S., Ferreira de Oliveira, J. M. P., Dias, M. C., Silva, A. M. S. & Santos, C. Antioxidant mechanisms to counteract TiO2-nanoparticles toxicity in wheat leaves and roots are organ dependent. *J. Hazard. Mater.* **380**, 120889 (2019).
192. Wang, Z. *et al.* Xylem- and phloem-based transport of CuO nanoparticles in maize (Zea mays L.). *Environ. Sci. Technol.* **46**, 4434–4441 (2012).
193. Shahid, M. *et al.* Foliar heavy metal uptake, toxicity and detoxification in plants: A comparison of foliar and root metal uptake. *J. Hazard. Mater.* **325**, 36–58 (2016).
194. Wang, J. *et al.* Phytostimulation of poplars and Arabidopsis exposed to silver nanoparticles and Ag+ at sublethal concentrations. *Environ. Sci. Technol.* **47**, 5442–5449 (2013).
195. Musante, C. & White, J. C. Toxicity of silver and copper to Cucurbita pepo: Differential effects of nano and bulk-size particles. *Environ. Toxicol.* **27**, 510–517 (2012).
196. Wu, Y. X. & von Tiedemann, A. Impact of fungicides on active oxygen species and antioxidant enzymes in spring barley (Hordeum vulgare L.) exposed to ozone. *Environ. Pollut.* **116**, 37–47 (2002).
197. Stewart, R. R. C. & Bewley, J. D. Lipid Peroxidation Associated with Accelerated Aging of Soybean Axes. *Plant Physiol.* **65**, 245–248 (2008).
198. Hong, J. *et al.* Evidence of translocation and physiological impacts of foliar applied CeO2 nanoparticles on cucumber (Cucumis sativus) plants. *Environ. Sci. Technol.* **48**, 4376–4385 (2014).
199. Singh, R., Upadhyay, A. K. & Singh, D. P. Regulation of oxidative stress and mineral nutrient status by selenium in arsenic treated crop plant Oryza sativa. *Ecotoxicol. Environ. Saf.* **148**, 105–113 (2018).

200. BEUTLER, E., DURON, O. & KELLY, B. M. Improved method for the determination of blood glutathione. *J. Lab. Clin. Med.* **61**, 882–888 (1963).

201. Cattani, D. *et al.* Developmental exposure to glyphosate-based herbicide and depressive-like behavior in adult offspring: Implication of glutamate excitotoxicity and oxidative stress. *Toxicology* **387**, 67–80 (2017).

202. Nel, A. Toxic Potential of Materials at the Nanolevel. *Science (80-.).* **311**, 622–627 (2006).

203. Colvin, V. L. The potential environmental impact of engineered nanomaterials. *Nat. Biotechnol.* **21**, 1166–1170 (2003).

204. Tortella, G. R. *et al.* Silver nanoparticles: Toxicity in model organisms as an overview of its hazard for human health and the environment. *Journal of Hazardous Materials* **390**, 121974 (2020).

205. Guan, P. *et al.* Recent Progress in Silver Nanowires: Synthesis and Applications. *Nanosci. Nanotechnol. Lett.* **10**, 155–166 (2018).

206. Jones, R., Draheim, R. & Roldo, M. Silver Nanowires: Synthesis, Antibacterial Activity and Biomedical Applications. *Appl. Sci.* **8**, 673 (2018).

207. Hu, L., Kim, H. S., Lee, J. Y., Peumans, P. & Cui, Y. Scalable coating and properties of transparent, flexible, silver nanowire electrodes. *ACS Nano* **4**, 2955–2963 (2010).

208. Toybou, D., Celle, C., Aude-Garcia, C., Rabilloud, T. & Simonato, J.-P. A toxicology-informed, safer by design approach for the fabrication of transparent electrodes based on silver nanowires. *Environ. Sci. Nano* **6**, 684–694 (2019).

209. H. Müller, K. *et al.* PH-dependent toxicity of high aspect ratio ZnO nanowires in macrophages due to intracellular dissolution. *ACS Nano* **4**, 6767–6779 (2010).

210. George, S. *et al.* Surface defects on plate-shaped silver nanoparticles contribute to its hazard potential in a fish gill cell line and zebrafish embryos. *ACS Nano* **6**, 3745–3759 (2012).

211. Riviere, J. E. *et al.* Modeling gold nanoparticle biodistribution after arterial infusion into perfused tissue: effects of surface coating, size and protein corona. *Nanotoxicology* **12**, 1093–1112 (2018).

212. Ji, Z. *et al.* Designed synthesis of CeO 2 nanorods and nanowires for studying toxicological effects of high aspect ratio nanomaterials. *ACS Nano* **6**, 5366–5380 (2012).

213. Bianchi, M. G. *et al.* Length-dependent toxicity of TiO2 nanofibers: mitigation via shortening. *Nanotoxicology* **14**, 433–452 (2020).

214. Kuo, C. W., Lai, J. J., Wei, K. H. & Chen, P. Studies of surface-modified gold nanowires inside living cells. *Adv. Funct. Mater.* **17**, 3707–3714 (2007).

215. Park, E. J. *et al.* Comparison of the toxicity of aluminum oxide nanorods with different aspect ratio. *Arch. Toxicol.* **89**, 1771–1782 (2015).

216. Scanlan, L. D. *et al.* Silver nanowire exposure results in internalization and

toxicity to daphnia magna. *ACS Nano* **7**, 10681–10694 (2013).

217. Wang, F. *et al.* Length and diameter-dependent phagocytosis and cytotoxicity of long silver nanowires in macrophages. *Chemosphere* **237**, 124565 (2019).

218. Safi, M. *et al.* Interactions between Magnetic Nanowires and Living Cells: Uptake, Toxicity, and Degradation. *ACS Nano* **5**, 5354–5364 (2011).

219. Moon, J., Kwak, J. Il & An, Y. J. The effects of silver nanomaterial shape and size on toxicity to Caenorhabditis elegans in soil media. *Chemosphere* **215**, 50–56 (2019).

220. Qiu, Y. *et al.* Surface chemistry and aspect ratio mediated cellular uptake of Au nanorods. *Biomaterials* **31**, 7606–7619 (2010).

221. Wu, J., Wang, G., Vijver, M. G., Bosker, T. & Peijnenburg, W. J. G. M. Foliar versus root exposure of AgNPs to lettuce: Phytotoxicity, antioxidant responses and internal translocation. *Environ. Pollut.* **261**, 114117 (2020).

222. Chithrani, B. D., Ghazani, A. A. & Chan, W. C. W. Determining the size and shape dependence of gold nanoparticle uptake into mammalian cells. *Nano Lett.* **6**, 662–668 (2006).

223. Chae, Y. & An, Y. J. Toxicity and transfer of polyvinylpyrrolidone-coated silver nanowires in an aquatic food chain consisting of algae, water fleas, and zebrafish. *Aquat. Toxicol.* **173**, 94–104 (2016).

224. Fan, W., Lu, H. & Wang, W. X. Aging Influences on the Biokinetics of Functional TiO2 Nanoparticles with Different Surface Chemistries in Daphnia magna. *Environ. Sci. Technol.* **52**, 7901–7909 (2018).

225. Jiang, C., Castellon, B. T., Matson, C. W., Aiken, G. R. & Hsu-Kim, H. Relative Contributions of Copper Oxide Nanoparticles and Dissolved Copper to Cu Uptake Kinetics of Gulf Killifish (Fundulus grandis) Embryos. *Environ. Sci. Technol.* **51**, 1395–1404 (2017).

226. Shao, Z. & Wang, W. X. Biodynamics of Silver Nanoparticles in an Estuarine Oyster Revealed by 110mAgNP Tracing. *Environ. Sci. Technol.* **54**, 965–974 (2020).

227. Dang, F., Wang, Q., Cai, W., Zhou, D. & Xing, B. Uptake kinetics of silver nanoparticles by plant: relative importance of particles and dissolved ions. *Nanotoxicology* 1–13 (2020). doi:10.1080/17435390.2020.1735550

228. Zhai, Y., Hunting, E. R., Wouterse, M., Peijnenburg, W. J. G. M. & Vijver, M. G. Importance of exposure dynamics of metal-based nano-ZnO, -Cu and -Pb governing the metabolic potential of soil bacterial communities. *Ecotoxicol. Environ. Saf.* **145**, 349–358 (2017).

229. Butz, S. V., Pinckney, J. L., Apte, S. C. & Lead, J. R. Uptake and impact of silver nanoparticles on the growth of an estuarine dinoflagellate, Prorocentrum minimum. *NanoImpact* **15**, 100181 (2019).

230. Akter, M. *et al.* A systematic review on silver nanoparticles-induced cytotoxicity: Physicochemical properties and perspectives. *J. Adv. Res.* **9**, 1–16 (2018).

231. Li, X., Lenhart, J. J. & Walker, H. W. Aggregation kinetics and dissolution of coated silver nanoparticles. *Langmuir* **28**, 1095–1104 (2012).

232. Römer, I. *et al.* Aggregation and dispersion of silver nanoparticles in exposure media for aquatic toxicity tests. *J. Chromatogr. A* **1218**, 4226–4233 (2011).

233. Yang, X. *et al.* Mechanism of silver nanoparticle toxicity is dependent on dissolved silver and surface coating in caenorhabditis elegans. *Environ. Sci. Technol.* **46**, 1119–1127 (2012).

234. Nguyen, K. C. *et al.* Comparison of toxicity of uncoated and coated silver nanoparticles. *J. Phys. Conf. Ser.* **429**, 012025 (2013).

235. Miller, E. L., Nason, S. L., Karthikeyan, K. G. & Pedersen, J. A. Root Uptake of Pharmaceuticals and Personal Care Product Ingredients. *Environ. Sci. Technol.* **50**, 525–541 (2016).

236. Medina-Velo, I. A., Peralta-Videa, J. R. & Gardea-Torresdey, J. L. Assessing plant uptake and transport mechanisms of engineered nanomaterials from soil. *MRS Bull.* **42**, 379–383 (2017).

237. Song, M. M. *et al.* Cytotoxicity and cellular uptake of iron nanowires. *Biomaterials* **31**, 1509–1517 (2010).

238. Lowry, G. V., Avellan, A. & Gilbertson, L. M. Opportunities and challenges for nanotechnology in the agri-tech revolution. *Nat. Nanotechnol.* **14**, 517–522 (2019).

239. *Silver Nanoparticles Market Size | Global Industry Report, 2012-2022. Grand View Research, Inc.: San Francisco, CA* (2015).

240. Rui, M. *et al.* Phytotoxicity of Silver Nanoparticles to Peanut (Arachis hypogaea L.): Physiological Responses and Food Safety. *ACS Sustain. Chem. Eng.* **5**, 6557–6567 (2017).

241. Pu, S., Yan, C., Huang, H., Liu, S. & Deng, D. Toxicity of nano-CuO particles to maize and microbial community largely depends on its bioavailable fractions. *Environ. Pollut.* **255**, 113248 (2019).

242. Das, P. *et al.* Nano-based soil conditioners eradicate micronutrient deficiency: soil physicochemical properties and plant molecular responses. *Environ. Sci. Nano* (2021). doi:10.1039/d1en00551k

243. Gao, X. *et al.* Effect of Soil Organic Matter, Soil pH, and Moisture Content on Solubility and Dissolution Rate of CuO NPs in Soil. *Environ. Sci. Technol.* **53**, 4959–4967 (2019).

244. Jośko, I., Kusiak, M. & Oleszczuk, P. The chronic effects of CuO and ZnO nanoparticles on Eisenia fetida in relation to the bioavailability in aged soils. *Chemosphere* **266**, 128982 (2021).

245. Gao, X. *et al.* CuO Nanoparticle Dissolution and Toxicity to Wheat (Triticum aestivum) in Rhizosphere Soil. *Environ. Sci. Technol.* **52**, 2888–2897 (2018).

246. Zhang, H. *et al.* Silver Nanoparticles Alter Soil Microbial Community Compositions and Metabolite Profiles in Unplanted and Cucumber-Planted Soils. *Environ. Sci. Technol.* **54**, 3334–3342 (2020).

247. Ge, Y. *et al.* Soybean Plants Modify Metal Oxide Nanoparticle Effects on Soil Bacterial Communities. *Environ. Sci. Technol.* **48**, 13489–13496 (2014).

248. Gao, X., Spielman-Sun, E., Rodrigues, S. M., Casman, E. A. & Lowry, G. V. Time and Nanoparticle Concentration Affect the Extractability of Cu from CuO NP-Amended Soil. *Environ. Sci. Technol.* **51**, 2226–2234 (2017).

249. Zhang, W., Dan, Y., Shi, H. & Ma, X. Effects of Aging on the Fate and Bioavailability of Cerium Oxide Nanoparticles to Radish (Raphanus sativus L.) in Soil. *ACS Sustain. Chem. Eng.* **4**, 5424–5431 (2016).

250. Montes de Oca-Vásquez, G. *et al.* Environmentally relevant concentrations of silver nanoparticles diminish soil microbial biomass but do not alter enzyme activities or microbial diversity. *J. Hazard. Mater.* **391**, 122224 (2020).

251. Grün, A. L. *et al.* Impact of silver nanoparticles (AgNP) on soil microbial community depending on functionalization, concentration, exposure time, and soil texture. *Environ. Sci. Eur.* **31**, 1–22 (2019).

252. Schlich, K. & Hund-Rinke, K. Influence of soil properties on the effect of silver nanomaterials on microbial activity in five soils. *Environ. Pollut.* **196**, 321–330 (2015).

253. Wang, Z., Yue, L., Dhankher, O. P. & Xing, B. Nano-enabled improvements of growth and nutritional quality in food plants driven by rhizosphere processes. *Environment International* **142**, 105831 (2020).

254. Vitali, F. *et al.* Environmental pollution effects on plant microbiota: the case study of poplar bacterial-fungal response to silver nanoparticles. *Appl. Microbiol. Biotechnol. 2019 10319* **103**, 8215–8227 (2019).

255. Klein, C. L. *et al. NM-Series of Representative Manufactured Nanomaterials NM-300 Silver Characterisation, Stability, Homogeneity*. doi:10.2788/23079

256. Hui, J., O'Dell, Z. J., Rao, A. & Riley, K. R. In Situ Quantification of Silver Nanoparticle Dissolution Kinetics in Simulated Sweat Using Linear Sweep Stripping Voltammetry. *Environ. Sci. Technol.* (2019). doi:10.1021/acs.est.9b04151

257. Das, P. *et al.* Mechanism of toxicity and transformation of silver nanoparticles: Inclusive assessment in earthworm-microbe-soil-plant system. *Geoderma* **314**, 73–84 (2018).

258. Cruz, N. C. *et al.* Dissolution of Ag Nanoparticles in Agricultural Soils and Effects on Soil Exoenzyme Activities. *Environments* **8**, 22 (2021).

259. Molleman, B. & Hiemstra, T. Time, pH, and size dependency of silver nanoparticle dissolution: The road to equilibrium. *Environ. Sci. Nano* **4**, 1314–1327 (2017).

260. Adamczyk, Z., Oćwieja, M., Mrowiec, H., Walas, S. & Lupa, D. Oxidative dissolution of silver nanoparticles: A new theoretical approach. *J. Colloid Interface Sci.* **469**, 355–364 (2016).

261. Lowry, G. V. *et al.* Long-Term Transformation and Fate of Manufactured Ag Nanoparticles in a Simulated Large Scale Freshwater Emergent Wetland. *Environ. Sci. Technol.* **46**, 7027–7036 (2012).

262. Settimio, L. *et al.* Fate and lability of silver in soils: Effect of ageing. *Environ. Pollut.* **191**, 151–157 (2014).

263. Carbone, S. *et al.* Bioavailability and biological effect of engineered silver nanoparticles in a forest soil. *J. Hazard. Mater.* **280**, 89–96 (2014).

264. Li, N., Li, X., Shi, Z. Y., Fan, X. Y. & Zhou, Z. W. Bacterial communities, potential pathogens and antibiotic resistance genes of silver-loaded stainless steel pipe wall biofilm in domestic hot water system. *J. Water Process Eng.* **40**, 101935 (2021).

265. Zeng, X. Y., Li, S. W., Leng, Y. & Kang, X. H. Structural and functional responses of bacterial and fungal communities to multiple heavy metal exposure in arid loess. *Sci. Total Environ.* **723**, 138081 (2020).

266. Ge, Y., Schimel, J. P. & Holdena, P. A. Identification of soil bacteria susceptible to TiO2 and ZnO nanoparticles. *Appl. Environ. Microbiol.* **78**, 6749–6758 (2012).

267. Ward, N. L. *et al.* Three genomes from the phylum Acidobacteria provide insight into the lifestyles of these microorganisms in soils. *Appl. Environ. Microbiol.* **75**, 2046–2056 (2009).

268. Bergmann, F. *et al.* Genomic insights into the metabolic potential of the polycyclic aromatic hydrocarbon degrading sulfate-reducing Deltaproteobacterium N47. *Environ. Microbiol.* **13**, 1125–1137 (2011).

269. Zhai, Y. *et al.* Interaction between a nano-formulation of atrazine and rhizosphere bacterial communities: atrazine degradation and bacterial community alterations. *Environ. Sci. Nano* **7**, 3372–3384 (2020).

270. Soil Analysis: An Interpretation Manual - Google 图书. Available at: https://books.google.nl/books?hl=zh-CN&lr=&id=pWR1vUWbEhEC&oi=fnd&pg=PR5&dq=Soil+Analysis:+An+Interpretation+Manual&ots=a_w5lEm_ZA&sig=gcDEzbQZXqg0AlsgxdM8LMn-83M#v=onepage&q=Soil Analysis%3A An Interpretation Manual&f=false. (Accessed: 23rd October 2020)

271. Walkley, A. & Black, I. A. An examination of the degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. *Soil Sci.* **37**, 29–38 (1934).

272. Hendershot, W. H. & Duquette, M. A Simple Barium Chloride Method for Determining Cation Exchange Capacity and Exchangeable Cations. *Soil Sci. Soc. Am. J.* **50**, 605–608 (1986).

273. Nowack, B. *et al.* Potential scenarios for nanomaterial release and subsequent alteration in the environment. *Environmental Toxicology and Chemistry* **31**, 50–59 (2012).

274. Hu, J. *et al.* TiO2 nanoparticle exposure on lettuce (: Lactuca sativa L.): Dose-dependent deterioration of nutritional quality. *Environ. Sci. Nano* **7**, 501–513 (2020).

275. Larue, C. *et al.* Innovative combination of spectroscopic techniques to reveal nanoparticle fate in a crop plant. *Spectrochim. Acta - Part B At. Spectrosc.* **119**,

17–24 (2016).

276. Servin, A. D. *et al.* Synchrotron micro-XRF and micro-XANES confirmation of the uptake and translocation of TiO2 nanoparticles in cucumber (Cucumis sativus) plants. *Environ. Sci. Technol.* **46**, 7637–7643 (2012).

277. Yang, J. *et al.* Alteration of Crop Yield and Quality of Wheat upon Exposure to Silver Nanoparticles in a Life Cycle Study. *J. Agric. Food Chem.* **66**, 2589–2597 (2018).

278. Servin, A. D. *et al.* Synchrotron verification of TiO2 accumulation in cucumber fruit: A possible pathway of TiO2 nanoparticle transfer from soil into the food chain. *Environ. Sci. Technol.* **47**, 11592–11598 (2013).

279. Du, W. *et al.* TiO2 and ZnO nanoparticles negatively affect wheat growth and soil enzyme activities in agricultural soil. *J. Environ. Monit.* **13**, 822–828 (2011).

280. Larue, C. *et al.* Accumulation, translocation and impact of TiO2 nanoparticles in wheat (Triticum aestivum spp.): Influence of diameter and crystal phase. *Sci. Total Environ.* **431**, 197–208 (2012).

281. Yan, N. & Wang, W. X. Novel Imaging of Silver Nanoparticle Uptake by a Unicellular Alga and Trophic Transfer to Daphnia magna. *Environ. Sci. Technol.* **55**, 5143–5151 (2021).

282. Chen, X., Zhu, Y., Yang, K., Zhu, L. & Lin, D. Nanoparticle TiO2 size and rutile content impact bioconcentration and biomagnification from algae to daphnia. *Environ. Pollut.* **247**, 421–430 (2019).

283. Zhu, X., Wang, J., Zhang, X., Chang, Y. & Chen, Y. Trophic transfer of TiO2 nanoparticles from daphnia to zebrafish in a simplified freshwater food chain. *Chemosphere* **79**, 928–933 (2010).

284. Judy, J. D., Unrine, J. M. & Bertsch, P. M. Evidence for biomagnification of gold nanoparticles within a terrestrial food chain. *Environ. Sci. Technol.* **45**, 776–781 (2011).

285. Judy, J. D., Unrine, J. M., Rao, W. & Bertsch, P. M. Bioaccumulation of gold nanomaterials by Manduca sexta through dietary uptake of surface contaminated plant tissue. *Environ. Sci. Technol.* **46**, 12672–12678 (2012).

286. Ma, Y. *et al.* Trophic Transfer and Transformation of CeO2 Nanoparticles along a Terrestrial Food Chain: Influence of Exposure Routes. *Environ. Sci. Technol.* **52**, 7921–7927 (2018).

287. Dai, Y. *et al.* Transfer and transformation of CeO2 NPs along a terrestrial trophic food chain. *Environ. Sci. Nano* **7**, 588–598 (2020).

288. Hawthorne, J. *et al.* Particle-Size Dependent Accumulation and Trophic Transfer of Cerium Oxide through a Terrestrial Food Chain. *Environ. Sci. Technol.* **48**, 13102–13109 (2014).

289. Majumdar, S. *et al.* Cerium Biomagnification in a Terrestrial Food Chain: Influence of Particle Size and Growth Stage. *Environ. Sci. Technol.* **50**, 6782–6792 (2016).

290. De La Torre Roche, R. *et al.* Terrestrial Trophic Transfer of Bulk and Nanoparticle La2O3 Does Not Depend on Particle Size. *Environ. Sci. Technol.* **49**, 11866–11874 (2015).

291. Servin, A. D. *et al.* Weathering in soil increases nanoparticle CuO bioaccumulation within a terrestrial food chain. *Nanotoxicology* **11**, 98–111 (2017).

292. Sharifan, H., Ma, X., Moore, J. M. C., Habib, M. R. & Evans, C. Zinc Oxide Nanoparticles Alleviated the Bioavailability of Cadmium and Lead and Changed the Uptake of Iron in Hydroponically Grown Lettuce (Lactuca sativa L. var. Longifolia). *ACS Sustain. Chem. Eng.* **7**, 16401–16409 (2019).

293. Sharifan, H., Wang, X. & Ma, X. Impact of nanoparticle surface charge and phosphate on the uptake of coexisting cerium oxide nanoparticles and cadmium by soybean (Glycine max. (L.) merr.). *Int. J. Phytoremediation* **22**, 305–312 (2020).

294. Liu, J. *et al.* TiO2 nanoparticles in irrigation water mitigate impacts of aged Ag nanoparticles on soil microorganisms, Arabidopsis thaliana plants, and Eisenia fetida earthworms. *Environ. Res.* **172**, 202–215 (2019).

295. Mtisi, M. & Gwenzi, W. Evaluation of the phytotoxicity of coal ash on lettuce (Lactuca sativa L.) germination, growth and metal uptake. *Ecotoxicol. Environ. Saf.* **170**, 750–762 (2019).

296. RASMUSSEN Kirsten; *et al. Titanium dioxide, NM-100, NM-101, NM-102, NM-103, NM-104, NM-105:: Characterisation and Physico-Chemical Properties.* (2014). doi:10.2788/79554

297. Dang, F. *et al.* Discerning the Sources of Silver Nanoparticle in a Terrestrial Food Chain by Stable Isotope Tracer Technique. *Environ. Sci. Technol.* **53**, 3802–3810 (2019).

298. Wu, J., Yu, Q., Bosker, T., Vijver, M. G. & Peijnenburg, W. J. G. M. Quantifying the relative contribution of particulate versus dissolved silver to toxicity and uptake kinetics of silver nanowires in lettuce: impact of size and coating. *Nanotoxicology* **14**, 1399–1414 (2020).

299. Unrine, J. M., Shoults-Wilson, W. A., Zhurbich, O., Bertsch, P. M. & Tsyusko, O. V. Trophic transfer of Au nanoparticles from soil along a simulated terrestrial food chain. *Environ. Sci. Technol.* **46**, 9753–9760 (2012).

300. Xiong, T. *et al.* Copper Oxide Nanoparticle Foliar Uptake, Phytotoxicity, and Consequences for Sustainable Urban Agriculture. *Environ. Sci. Technol.* **51**, 5242–5251 (2017).

301. Hartono, D., Lioe, B., Zhang, Y., Li, B. & Yu, J. Impacts of particulate matter (PM2.5) on the behavior of freshwater snail Parafossarulus striatulus. *Sci. Rep.* **7**, 1–8 (2017).

302. Silva, P. V. *et al.* Toxicokinetics of pristine and aged silver nanoparticles in: Physa acuta. *Environ. Sci. Nano* **7**, 3849–3868 (2020).

303. Schleh, C. *et al.* Size and surface charge of gold nanoparticles determine absorption across intestinal barriers and accumulation in secondary target

organs after oral administration. *Nanotoxicology* **6**, 36–46 (2012).

304. Dang, F., Huang, Y., Wang, Y., Zhou, D. & Xing, B. Transfer and toxicity of silver nanoparticles in the food chain. *Environ. Sci. Nano* (2021). doi:10.1039/D0EN01190H

305. Kaloyianni, M. *et al.* Magnetite nanoparticles effects on adverse responses of aquatic and terrestrial animal models. *J. Hazard. Mater.* **383**, 121204 (2020).

306. Song, Y. *et al.* Uptake and adverse effects of polyethylene terephthalate microplastics fibers on terrestrial snails (Achatina fulica) after soil exposure. *Environ. Pollut.* **250**, 447–455 (2019).

307. Chae, Y. & An, Y. J. Nanoplastic ingestion induces behavioral disorders in terrestrial snails: Trophic transfer effects: Via vascular plants. *Environ. Sci. Nano* **7**, 975–983 (2020).

308. Kwak, J. Il & An, Y. J. Trophic transfer of silver nanoparticles from earthworms disrupts the locomotion of springtails (Collembola). *J. Hazard. Mater.* **315**, 110–116 (2016).

309. Mehennaoui, K. *et al.* Gammarus fossarum (Crustacea, Amphipoda) as a model organism to study the effects of silver nanoparticles. *Sci. Total Environ.* **566–567**, 1649–1659 (2016).

310. da Costa Araújo, A. P. & Malafaia, G. Microplastic ingestion induces behavioral disorders in mice: A preliminary study on the trophic transfer effects via tadpoles and fish. *J. Hazard. Mater.* **401**, 123263 (2021).

311. Zou, X., Shi, J. & Zhang, H. Coexistence of silver and titanium dioxide nanoparticles: Enhancing or reducing environmental risks? *Aquat. Toxicol.* **154**, 168–175 (2014).

312. Haghighat, F., Kim, Y., Sourinejad, I., Yu, I. J. & Johari, S. A. Titanium dioxide nanoparticles affect the toxicity of silver nanoparticles in common carp (Cyprinus carpio). *Chemosphere* **262**, 127805 (2021).

313. Ma, T., Wang, M., Gong, S. & Tian, B. Impacts of Sediment Organic Matter Content and pH on Ecotoxicity of Coexposure of TiO2 Nanoparticles and Cadmium to Freshwater Snails Bellamya aeruginosa. *Arch. Environ. Contam. Toxicol.* **72**, 153–165 (2017).

314. Fan, W. H., Cui, M. M., Shi, Z. W., Tan, C. & Yang, X. P. Enhanced oxidative stress and physiological damage in daphnia magna by copper in the presence of Nano-TiO 2. *J. Nanomater.* **2012**, (2012).

315. Scheringer, M. Nanoecotoxicology: Environmental risks of nanomaterials. *Nature Nanotechnology* **3**, 322–323 (2008).

316. Savolainen, K. *et al. Nanosafety in Europe 2015–2025: Towards Safe and Sustainable Nanomaterials and Nanotechnology Innovations, Finnish Institute of Occupational Health.* (2013).

317. Athanassiou, C. G. *et al.* Nanoparticles for pest control: current status and future perspectives. *Journal of Pest Science* **91**, 1–15 (2018).